

COATINGS AND ENAMELS

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EFFECT OF A COMPLEX OF ALIOVALENT CATIONS ON PROCESSES IN AN ENAMEL MELT – LOW-CARBON STEEL SYSTEM

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The interrelationship of the corrosion activity of enamel melts containing a complex adhesion activator, their specific electric conductivity, and the strength of the adhesion of the corresponding coatings is investigated. The partial and integral effects of aliovalent oxides on the properties of prime vitreous enamels are determined. The principles of the electrochemical theory of adhesion of enamel coatings on steel, using a complex adhesion activator, are confirmed.

The adhesion of enamel coatings on steel is the result of the combined action of mechanical adhesion forces and chemical bonds. Numerous investigations, specifically those performed at the Kharkov Polytechnical Institute (now the National Technical University “Kharkov Polytechnical Institute”), have shown that mechanical bonding is due to micro- and macro-nonuniformities which arise on the surface of the steel as a result of electrochemical corrosion of the steel by the enamel melt during firing of the coatings [1, 2]. To ensure selective erosion of steel, the enamel melt must possess a certain optimal value of the specific electric conductivity [3].

According to the currently held ideas about the role of the intensity of corrosion processes at the point of contact between steel and the enamel melt in achieving strong bonding of the coating on the metal, a special role is given to aliovalent oxides [4]. Introducing into prime enamels adhesion activators increases the electrochemical effect of the enamel melt on the steel; this results in a large increase of the surface area and, correspondingly, increases the bonding strength of the coatings on a metal base.

The existing theoretical works in this direction concern the analysis of the importance of individual transition-metal oxides on the processes indicated. At the same time, in enameling practice several bonding oxides are increasingly introduced simultaneously into the prime enamel, especially when prime enamels are produced with a lower firing temperature. The electrochemical processes occurring in the

steel – enamel melt system containing several aliovalent cations simultaneously will be much more complicated and diverse compared with the steel – enamel coating system containing only one adhesion activator because the electrode potentials of the cations will be variable under conditions of varying temperature and properties of the melt. For this reason, it is necessary to determine the mechanisms of these processes when a complex of adhesion activators is present in the enamel melt in order to understand better the nature of the adhesion of a glass coating on metal. This is possible only by making a comparative assessment of the partial and integral effect of aliovalent oxides on the corrosion activity, the specific electric conductivity of frit melts, and the adhesion strength of the corresponding coatings.

In this connection, our objective in the present work is to investigate the partial and complex influence of cations on some of the main adhesion activators used in enameling on the strength of the interaction between the enamel melts and low-carbon steel.

To study the processes occurring when low-carbon steel comes into contact with enamel melt containing a complex of transition-metal cations, model glasses in the system $R_2O - RO - B_2O_3 - Al_2O_3 - SiO_2$ were synthesized. The contents of the main components of the glass were as follows (%²): 40 – 60 SiO_2 , 10 – 25 Na_2O , 10 – 20 B_2O_3 , 3 – 10 CaO , 1.5 – 5 Al_2O_3 , 0 – 5 TiO_2 .

The model glasses were melted in corundum crucibles in an electric furnace at 1200 – 1250°C. The optimal composi-

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² Here and below — the mass content.

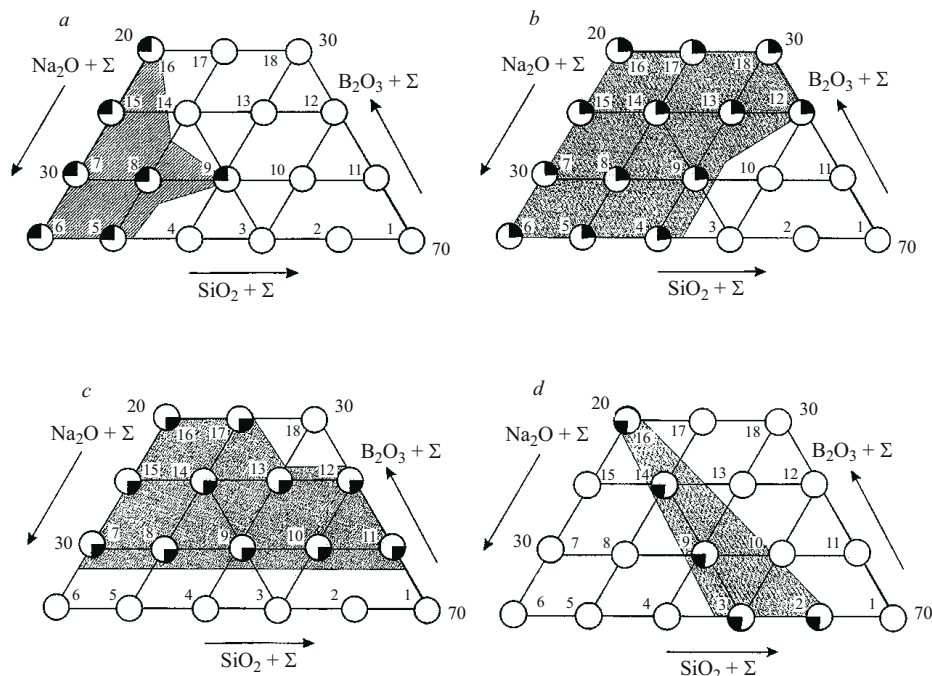


Fig. 1. Composition ranges in the pseudoternary system $\text{Na}_2\text{O} + \Sigma - \text{B}_2\text{O}_3 + \Sigma - \text{SiO}_2 + \Sigma$ ($\Sigma(\text{CaO} + \text{Al}_2\text{O}_3 + \text{TiO}_2) = 10\%$) with the preferred values of the properties: a) temperature of complete melting; b) wetting angle; c) surface tension; d) CLTE.

tion of the model glass No. 9 as a base for subsequent synthesis of prime frits (Fig. 1) was established according to the following requirements for the main properties:

no crystallization;

CLTE at 900°C in the range $(90 - 110) \times 10^{-7} \text{ K}^{-1}$;

surface tension $220 - 250 \text{ mN/m}$;

wetting at temperature 820°C not exceeding 15° ;

temperature of complete melting no higher than 850°C .

The partial and integral effect of adhesion activators introduced into the model glasses in amounts ranging from 0.5 to 12% on the corrosion activity and the specific electric conductivity of the their melts with respect to 08kp low-carbon steel in the temperature interval $600 - 1000^\circ\text{C}$ and on the adhesion strength of coatings of these melts on a metal substrate were studied.

The corrosion activity of the glass melt interacting with a metal substrate is determined by a gravimetric method according to the change in mass of metal samples as the samples are heated: according to the thickness of the destroyed layer of metal, according to the change in the diameter of a metal rod immersed in the melt, on the metal – melt – atmospheric boundary, or according to the change in the emf of a metal – melt system.

In the present work the corrosion activity of melts with respect to steel was determined by a procedure developed at the Kharkov Polytechnical Institute [2]. In this procedure 10 mm in diameter and 40 mm high rods consisting of 08kp low-carbon steel (GOST 24244-80) were immersed vertically into pre-homogenized melt and allowed to stand at a

constant temperature 1000°C for 3 h, after which the relative change Δd in the diameter of the rod was measured. This quantity characterized the corrosion activity of the enamel melt with respect to the steel indicated above. This method was chosen because, according to the data of [1], the electrochemical corrosion of steel under the action of a glass melt occurs with oxygen depolarization, and consequently the greatest dissolution of the metal will be observed at the melt surface – air boundary.

The corrosion of metals and enamel melts, which like most oxide glass-forming melts are ionic, is predominantly of electrochemical nature. The prerequisites for electrochemical corrosion to occur at the point of contact between enamel melt and steel are thermodynamic instability of iron and glass-forming melts, ionic conductivity of such melts, which increases rapidly with temperature, micro- and macro-nonuniformity of the steel surface, and the presence of compounds which could be depolarizers during cathodic reactions, specifically, O_2 and H_2O [3, 4], in the furnace atmosphere and glass melts.

The data obtained (Fig. 2a) show that copper oxide in amounts up to 1% has the greatest partial effect on increasing the corrosion activity of melts. Melt action on steel increases with CoO and NiO contents up to 2%. At higher MeO ($\text{Me} - \text{Cu, Ni, Co}$) content the corrosion processes occurring on the metal – melt – atmospheric contact surface slow down as a result of the deposition of reducing metal particles, which was observed during a visual examination of the samples, especially in the case of compositions containing copper.

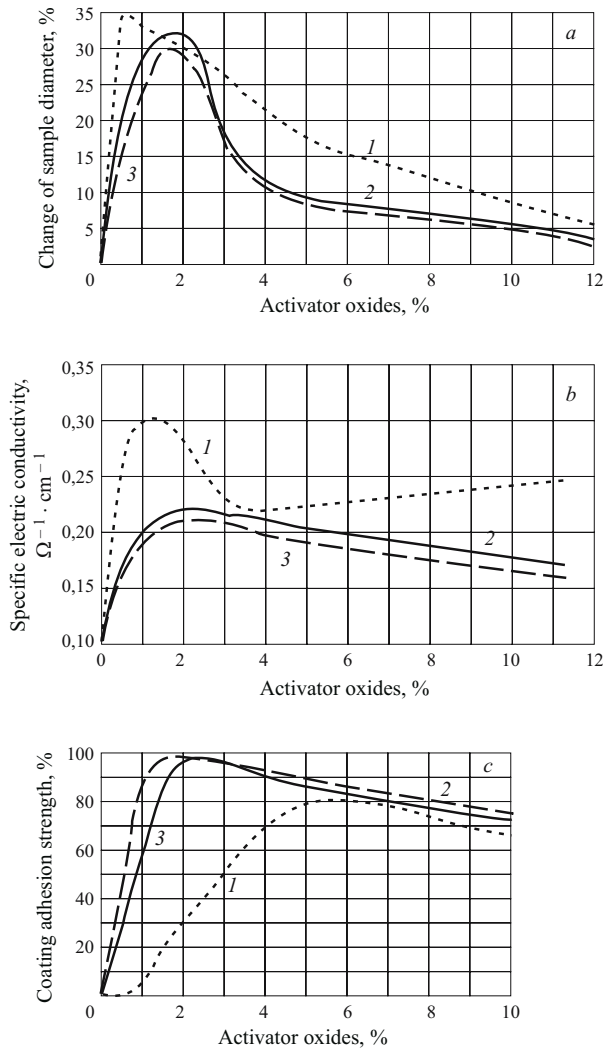


Fig. 2. Corrosion activity (a), specific electrical activity (b) of glass melts and adhesion strength of coatings (c) based on them versus activator oxide partial contents: 1) CuO; 2) CoO; 3) NiO.

L. D. Svirskii and L. L. Bragina have established that in studying the specific electrical conductivity, the corrosion activity, and the strength of adhesion of cobalt-, copper-, and nickel-containing enamel frits with partial content of bonding and activators there is a definite relation between these properties: definite values of the corrosion activity of the melts ($\Delta d = 30 - 32\%$) and the highest adhesion strength of coatings on steel (about 98%) correspond to optimal values of the specific electric conductivity of the melts ($0.214 - 0.218 \Omega^{-1} \cdot \text{cm}^{-1}$).

Compared with the dependences of the corrosion activity (see Fig. 2a) and the specific electrical conductivity (Fig. 2b) of the experimental frits which we investigated at 900°C on the partial content of MeO, it is obvious that their variations are similar (taking account of the reduction of transition metals at the melt – steel interphase boundary, as noted above) and therefore these properties are interrelated.

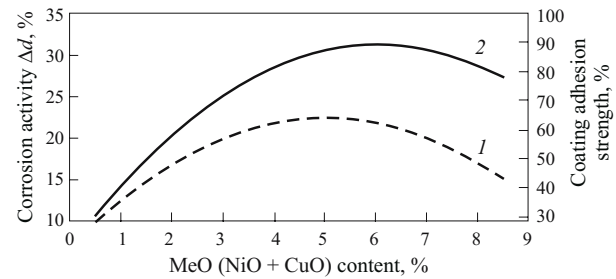


Fig. 3. Combined effect of adhesion activator oxides on the corrosion activity (1) of melts of the model frits and the adhesion strength (2) of the coatings based on them.

The study of the influence of the adhesion activators indicated above (for partial introduction of the activators) on the strength of the adhesion of the coatings consisting of these melts on low-carbon steel has established that the maximum adhesion strength is obtained when NiO and CoO in quantities up to 2% and CuO up to 6% are introduced. The character of the dependence of the adhesion strength of these coatings on the partial content of the adhesion activators (Fig. 2c) approaches closest to this dependence for the corrosion activity of the melts than for their specific electrical activity; apparently, this is due to passivation of the steel surface of the sample and the decrease, occurring at the same time, of the zone of active metal – melt interaction [5].

These data largely confirm the principles of the electrochemical theory of the adhesion of enamel coatings on steel, which were advanced in application to compositions with partial content of adhesion activators [3, 4].

It should be noted that the results obtained showed that cobalt and nickel oxides have a similar effect on the character of the interaction between enamel melt and a steel substrate and, ultimately, on the adhesion strength of prime coatings on metal. In this connection, and also in connection with the proposed possibility of using technogenic materials for delivering adhesion activators which do not contain expensive and scarce cobalt compounds, it became necessary to investigate the possibility of synthesizing coatings which contain only nickel and copper oxides introduced together.

The study of the integral effect of nickel and copper oxides on the corrosion activity of melts of the model frits and the adhesion strength of the corresponding prime coatings on low-carbon steel showed that the curves of both properties versus the total concentration $C_{\Sigma\text{MeO}}$ exhibit very similar behavior (Fig. 3): in both cases these parameters increase with $C_{\Sigma\text{MeO}}$, reaching maximum values for relatively close values of $C_{\Sigma\text{MeO}}$. This could mean that these properties are interrelated.

The maximum adhesion strength of coatings with 6% complex adhesion activator was achieved, in contrast to compositions containing only one adhesion activator, not with the highest corrosion activity of melt ($\Delta d = 24\%$) but rather at some optimal value corresponding to $\Delta d = 21\%$. This suggests that the adhesion strength in this case, in con-

trast to compositions with partial MeO content, is not only due to the electrochemical processes but it is also a consequence of the appearance of intermediate layers at the metal – coating boundary, which form with the participation of activator oxides. In this case, ferrosipinel compounds of the type MeFe_2O_4 form [6].

In summary, the characteristics of the partial and integral effect of aliovalent oxides on the corrosion activity and specific electrical conductivity of glass melts containing a complex adhesion activator and on the adhesion strength of the corresponding coatings on low-carbon steels have been determined. It has been found that the formation of intermediate layers on the boundary between a metal and a coating containing complex aliovalent cations plays a large role.

REFERENCES

1. L. D. Svirskii and L. L. Bragina, "Contribution to the question of adhesion of heat-resistant enamel coatings to metal," in: *Refractory and Heat-Resistant Coatings* [in Russian], Nauka, Leningrad (1969), pp. 68 – 72.
2. L. L. Bragina, *Refractory Silicate Coatings for Protecting Ferrous Metals, Author's Abstract of Doctoral Thesis* [in Russian], Kharkov (1988).
3. L. Bragina and A. Bondarenko, "Enamels for new enameling processes," *Smalto Porcellanato*, No. 1, 26 – 31 (2004).
4. A. Dietzel, *Emaillierung. Wissenschaftliche Grundlagen und Grundzüge der Technologie*, Berlin, New York (1981), pp. 168 – 390.
5. G. K. Voronov and L. L. Bragina, "Influence of the structure of steel on its interaction with silicate melts," in: *Scientific Proc. of the Ukrainian Scientific and Research Institute of Refractory Materials* [in Russian], No. 101, Karavella, Kharkov (2001), pp. 186 – 190.
6. Shirasaki Masahiro, "Reactions and adherence mechanism of Co and Ni on border between metal and enamel," *Chiba Kogyo Deigaku, Kenkyu Hokou*, No. 47, 340 (2000).